

Shock Chemistry of Sugars and Implications for Delivery by Meteorites

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October 2003

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This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Recent detection of the sugar glycolaldehyde in the interstellar molecular cloud Sagittarius B2(N) (Hollis *et al.* 2000) and models of its formation (Sorrell, 2001) have helped fuel the idea that biologically-relevant organic compounds can form easily in space and can be delivered to Earth or other planets by comets, meteorites, and asteroids. Glycolaldehyde is a useful bio-ingredient because it can polymerize into higher forms of carbohydrates, such as ribose, the sugar that makes up the backbone for RNA, and glucose, the sugar found in plant saps and fruits (Hollis *et al.* 2000; see Figure 1). Glycolaldehyde is reactive and can form various kinds of complex organic compounds; therefore, it may be an important ingredient for starting life on the early Earth. Its presence in space, while not ubiquitous, is an important clue for understanding the chemical routes that can lead to the formation of other molecules, both simple and complex.

Meteorites contain materials coalesced from dense molecular clouds during or prior to formation of the Solar System. Carbonaceous chondrites are of special interest to studies of the origin of life because they contain carbon-based compounds, such as amino acids (e.g. Pizzarello *et al.* 1991; Botta and Bada, 2002) and sugars (Cooper *et al.* 2001, 2002), essential constituents of terrestrial organisms. Dihydroxyacetone, sugar acids, and sugar alcohols have been identified in the Murchison and Murray meteorites (Cooper *et al.* 2001, 2002), and laboratory analyses of simple sugar mass spectra have suggested that similar features exist in Comet Halley spectra (Robinson and Wdowiak, 1994). While shock experiments have already been carried out to understand the effects of pressure and temperature on the chemistry of amino acids with relevance to their delivery to Earth by comets (e.g. Blank *et al.* 2001), to date, no experiments regarding the impact delivery and survivability of sugars have been done.

Here we propose studies that will focus on understanding how dimers of glycolaldehyde $(C_4H_8O_4)$ and dihydroxyacetone $(C_6H_{12}O_6)$, two of the simplest sugars (Table 1), react under the extreme pressures and temperatures of simulated terrestrial impact events. The existing two-stage light-gas gun at LLNL (e.g. Koch *et al.* 1990) can be used to carry out shock experiments of sugar solutions in a manner similar to that of Blank *et al.* (2001), and liquid or gas chromatography and mass spectrometry (LCMS, GCMS) can be used to identify the solutions'

end products (see Appendix A for a list of the experiments' components). It is likely that these sugars will break down, but they may form more complex molecules, such as ribose ($C_5H_{10}O_5$) or glucose ($C_6H_{12}O_6$), since sugars provide the carbon skeletons for many molecules. The latter outcome would be significant to understanding the delivery and subsequent shock chemistry of extraterrestrial bio-ingredients because it would show that these molecules could survive impact events to form more complicated molecules, in contrast to other reports (e.g. Chyba *et al.* 1990) but in support of the findings of Blank *et al.* (2001).

Current understanding of comet and asteroid impact mechanics is limited by computer modeling of impact structures and ejecta patterns (e.g. Melosh, 1989). Additional information can be gained by collecting geological material shocked by the impact event itself (e.g. Xie *et al.* 2003; Fisenko and Semjonova, 2001; Miura *et al.* 1990; Lambert, 1982) and by surveying the impact site, though it is highly speculative as to whether the crater is the result of a comet or asteroid impact. Typical impact velocities range from 11 km/sec (the escape velocity of Earth) to 72 km/sec (the escape velocity of the Solar System), with impact pressures ranging from 4 GPa (Lambert, 1982) to upwards of 65 GPa (Fisenko and Semjonova, 2001). These parameters can be duplicated to some extent in the gun lab; a 2 km/sec shot creates conditions on the sample capsule comparable to an oblique impact on Earth (45 GPa, 1000 °C; Cummings and Blank, 2003). However, extrapolating the timescale of the experiment (\Box s) to the timescale of an actual impact (ms to sec) (DeCarli *et al.* 2003) may be difficult, and it will be important to understand the influence of kinetics on the reaction chemistry of the sugars. For this reason and to understand the complicated chemistry of sugars in general, a collaborative investigation with George Cooper at NASA Ames is being proposed here.

At a minimum, 6 sample capsules should be prepared: 2 capsules with a solution of glycolaldehyde, 2 capsules with a solution of dihydroxyacetone, and 2 capsules with a solution of both sugars. In this manner, we can see the effects of the shock on each individual sugar in isolation and on both sugars together; a second shot will confirm (or not) the results of the first. The shots will be configured in the manner of Blank *et al.* (2001), and the shocked solutions will be similarly extracted. Analysis of the shocked liquids will be done by either LCMS (at LLNL in collaboration with Jennifer Blank) or by GCMS (at NASA Ames in collaboration with George Cooper), both giving elution times and chromatographic peaks with mass/charge ratios (m/z) representative of the molecule being analyzed in the liquid or gas phase, respectively. The

advantage of using GCMS is that the analytical method has already been developed by Cooper and his colleagues; the LCMS analytical protocol would have to be developed at LLNL. Unshocked solutions of the three combinations will be analyzed separately, as control experiments, for comparison to their shocked counterparts.

The survivability of molecules after delivery by comets, meteorites, and asteroids lends credence to the idea that the ingredients needed for life had non-terrestrial sources, supported by evidence that the early Earth may have been hostile to the formation of these molecules because its mantle was at-or-near its current oxidation state (e.g. Delano 2001). Understanding the impact flux of these objects (Zellner *et al.* in prep.) will better constrain the delivery mechanisms, efficiencies, and timeframes. The subsequent chemical interactions in favorable (i.e. reducing) areas, then, may have been localized and may have lead to the origin of life as soon as a "critical mass" of biomolecules was obtained, possibly independent of the terrestrial impact flux, though how these molecules actually interacted to form the first life is still unknown.

Acknowledgements: NEBZ thanks Oliver Botta and Nicholas Platts for critical reviews and Jennifer Blank for initial discussions and collaboration. This work was performed under the auspices of the U.S. Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

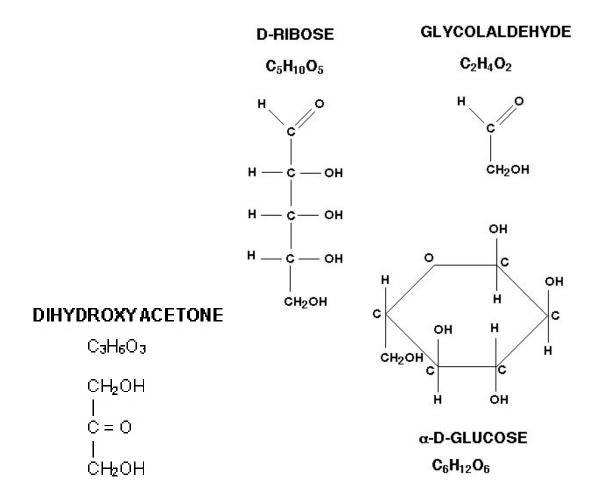


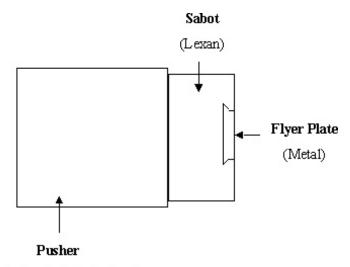
Figure 1. Comparison of glycolaldehyde and dihydroxyacetone to ribose and glucose.

	Glycolaldehyde (dimer)	Dihydroxyactone (dimer)
Molecular Formula	C ₄ H ₈ O ₄	$C_6H_{12}O_6$
Formula Mass	120.1 g mol ⁻¹	180.2 g mol ⁻¹
Solubility in H ₂ O (at 25 °C)	50 mg/mL	25 mg/mL
Melting Temperature	80 – 90 °C	$80-90$ $^{\circ}$ C

 $Table \ 1. \ Characteristics \ of glycolal dehyde \ and \ dihydroxyacetone, two \ of \ the \ simplest \ sugars.$

Appendix A: Components for a gun shot and sample analysis

Projectile (flyer + sabot + pusher)



(High-density Polyethylene)

Piston (in gun)

Pig (holds capsule during shot)

Target (capsule + plug = capsule assembly [stainless steel])

Slapper

Target (capsule) cleaning (to remove all contaminants)

Filling capsule with sugar solution(s)

Set screws and gold balls (for plugging capsule assembly)

Laser welding to seal capsule assembly

Setting the loaded capsule into the pig

Preparing the gun for the shot (incl. gun powder)

Monitoring shot (incl. set-up diagnostics, flash X-ray, laser trap)

Getting shot velocity, capsule temperature

Facing capsule after shot (incl. using ultrasonic depth gauge for measuring thickness of capsule)

Opening capsule

- 1. use treepanner designed by Tim (but not yet tested)
- 2. puncture faced side (but contents under pressure)

Extracting shocked solution: syringe

Analysis: LCMS or GCMS

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